

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 810 235 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
24.11.2004 Bulletin 2004/48

(51) Int Cl.7: **C08F 4/642, C08F 10/00**

(21) Application number: **97201629.9**

(22) Date of filing: **02.06.1997**

(54) **Polymerization catalyst**

Polymerisationskatalysator

Catalyseur de polymérisation

(84) Designated Contracting States:
DE ES NL PT

(30) Priority: **31.05.1996 US 656028**

(43) Date of publication of application:
03.12.1997 Bulletin 1997/49

(60) Divisional application:
01201212.6 / 1 125 951
01201211.8 / 1 125 950

(73) Proprietor: **Intevp SA**
Caracas 1070 A (VE)

(72) Inventors:
• **Diaz-Barrios, Antonio**
San Antonio de Los Altos (VE)
• **Liscano, Jose**
Piso 6, Apt C-61, Los Teques Edo.Miranda (VE)
• **Trujillo, Marianela**
Chalbaud, Coche, Caracas 1091 (VE)

- **Agrifoglio, Giuseppe**
Sorocaima, Baruta (VE)
- **Matos, Jose Orlando**
Apto. 16-A, Los Teques (VE)

(74) Representative: **van Westenbrugge, Andries et al**
Nederlandsch Octrooibureau
P.O. Box 29720
2502 LS The Hague (NL)

(56) References cited:
EP-A- 0 206 893 **EP-A- 0 501 741**
GB-A- 2 066 272 **US-A- 4 223 118**
US-A- 5 238 891

- **PATENT ABSTRACTS OF JAPAN vol. 014, no.**
417 (C-0756), 10 September 1990 & JP 02 158608
A (TOSOH CORP), 19 June 1990,

Remarks:

The file contains technical information submitted
after the application was filed and not included in this
specification

EP 0 810 235 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

BACKGROUND OF THE INVENTION

5 [0001] The invention relates to a polymerization catalyst, particularly to a polymerization catalyst for the polymerization of olefins.

[0002] Numerous processes are known in the art for polymerization of olefins such as ethylene into polyolefins such as polyethylene.

10 [0003] Parameters of concern during the polymerization of olefins include the yield of polyolefin, the melt flow index (MFI) of the polyolefin product, the bulk density of the polyolefin product, and the content of fines in the resulting polyolefin product. Numerous catalysts and processes are known in the art for polymerizing olefins so as to obtain polyolefins. The need remains, however, for a polymerization catalyst for polymerization of olefins which has good activity toward the polymerization reaction, while providing a final product with a desirable melt flow index and bulk density, and further while reducing the content of fines therein.

15 [0004] It is therefore the primary object of the present invention to provide a polymerization catalyst for polymerization of olefins which has enhanced activity toward the polymerization reaction so as to provide enhanced yield of polyolefin product with a desirable bulk density.

[0005] It is a further object of the present invention to provide an olefin polymerization catalyst wherein the polyolefin product has a reduced content of fines.

20 [0006] It is a further object of the present invention to provide an additive for an olefin polymerization catalyst which enhances the characteristics of the catalyst for polymerization of olefins.

[0007] Other objects and advantages of the present invention will appear hereinbelow.

SUMMARY OF THE INVENTION

25 [0008] In accordance with the present invention, the foregoing objects and advantages are readily attained. In accordance with the invention, an olefin polymerization catalyst is provided which comprises a halogen-containing magnesium compound; a titanium compound; and an additive selected from the group consisting of (a) a mixture of an aluminum alkoxide compound and polydimethylsiloxane, (b) an aluminosiloxane selected from the group consisting of
30 $[Al(OR')_2(OSiR''_3)]_m$, $[Al(OR')(OSiR''_3)_2]_p$, and $[Al(OSiR''_3)_3]_2$, wherein R' and R'' are alkyl or aryl groups having up to 12 carbons and m and p are any whole number greater than 1, and mixtures thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

35 [0009] A detailed description of preferred embodiments of the invention follows, with reference to the attached drawings, wherein:

FIGS. 1-5 illustrate embodiments of aluminosiloxanes additives according to the present invention.

DETAILED DESCRIPTION

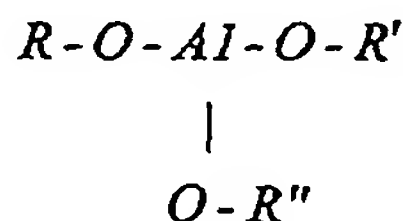
40 [0010] The invention relates to an olefin polymerization catalyst, especially to a catalyst for polymerization of olefins such as ethylene into polyolefins such as polyethylene.

45 [0011] The present polymerization catalyst is based upon Ziegler-Natta catalysts typically comprising a magnesium halide support and a titanium compound supported on the magnesium halide support. In accordance with the present invention, a series of additives have been developed which, when incorporated into the polymerization catalyst, provide enhanced activity and characteristics of the catalyst toward the polymerization reaction. In accordance with the invention, it has been found to be advantageous to incorporate an additive selected from the group consisting of a mixture of (a) a mixture of an aluminum alkoxide compound and polydimethylsiloxane, (b) an aluminosiloxane selected from the group consisting of
50 $[Al(OR')_2(OSiR''_3)]_m$, $[Al(OR')(OSiR''_3)_2]_p$, and $[Al(OSiR''_3)_3]_2$, wherein R' and R'' are alkyl or aryl groups having up to 12 carbons and m and p are any whole number greater than 1, and mixtures thereof so as to provide the olefin polymerization catalyst according to the present invention. A catalyst containing such an additive according to the present invention has been found to have excellent activity toward the polymerization reaction so as to provide an enhanced yield of polyolefin having desirable qualities, while using a relatively small amount of titanium supported on the magnesium, and further while providing a catalyst which results in a reduced amount of fines in the
55 resulting polyolefin product.

[0012] In accordance with the invention, the halogen containing magnesium compound may suitably be magnesium chloride, while the titanium compound may suitably be titanium chloride, especially titanium tetrachloride.

[0013] As set forth above, the series of additives which has been found in accordance with the invention to provide desirable characteristics in a polymerization catalyst includes an additive selected from the group consisting of (a) a mixture of an aluminum alkoxide compound and polydimethylsiloxane, (b) an aluminosiloxane selected from the group consisting of $[Al(OR')_2(OSiR''_3)]_m$, $[Al(OR')(OSiR''_3)_2]_p$, and $[Al(OSiR''_3)_3]_2$, wherein R' and R'' are alkyl or aryl groups having up to 12 carbons and m and p are any whole number greater than 1, and mixtures thereof.

[0014] One additive in accordance with the present invention, as set forth above, may suitably be a mixture of aluminum compound and polydimethylsiloxane. An aluminum alkoxide compound as used herein refers to an organic compound having the functionality



(wherein R, R' and R'' are the same or different hydrocarbyl radicals of not more than 12 carbon atoms), such as methyl, ethyl and isopropyl. Examples of particularly desirable aluminum alkoxide compounds for combination with polydimethylsiloxane in accordance with the invention include aluminum methoxide, aluminum ethoxide, aluminum isopropoxide and mixtures thereof.

[0015] In accordance with the present invention, when the additive is to be a mixture of aluminum alkoxide and polydimethylsiloxane, the polydimethylsiloxane preferably has a molecular weight of between 150 and 300,000, more preferably between 150 and 770. Relatively low molecular weight polydimethylsiloxane has been found in accordance with the invention to provide a catalyst having a better catalyst activity than those produced with higher molecular weight polydimethylsiloxane.

[0016] In further accordance with the invention, aluminosiloxane compounds have also been found to be particularly desirable additives to the catalyst in accordance with the present invention. As regards the aluminosiloxane compound in accordance with the present invention R' may preferably be selected from the group consisting of ethyl, propyl, isopropyl, n-butyl, isobutyl, t-butyl and mixtures thereof, while R'' is selected from the group consisting of methyl, phenyl, ethyl, propyl, isopropyl, t-butyl and mixtures thereof. The aluminosiloxane compound according to the invention has a ratio of Al:Si which is preferably 1:1, 1:2, or 1:3.

[0017] As set forth above, one preferable form of the aluminosiloxane compound is $[Al(OR')_2(OSiR''_3)]_m$. Two examples of this compound are shown in the drawings in FIGS. 1 and 2. In the example illustrated in FIGS. 1 and 2, R' is isopropyl, R'' is methyl, and the ratio of Al:Si is 1:1.

[0018] Referring to FIG. 3, another preferred aluminosiloxane compound is shown which corresponds to $[Al(OSiR''_3)_3]_2$, as set forth above. As shown in FIG. 3, R'' in this compound is methyl, and the ratio Al:Si is 1:3.

[0019] Referring to FIGS. 4 and 5, a further embodiment of an aluminosiloxane compound additive in accordance with the present invention is shown. In accordance with the illustrated embodiment, compounds are illustrated having the formula $[Al(OR')(OSiR''_3)_2]_p$. In the embodiment shown in FIGS. 4 and 5, R' is isopropyl, while R'' is methyl, and the ratio Al:Si is 1:2.

[0020] The olefin polymerization catalyst of the present invention preferably has a substantially monomodal and narrow particle size distribution which preferably has an average particle size of between 2 to 200 μm . Further, the catalyst preferably has an Al/Si molar ratio of between 0.1 to 300, more preferably between 0.33 to 1 (Al:Si between 1:1 to 1:3), especially when the additive is an aluminosiloxane compound.

[0021] Further, the catalyst according to the present invention preferably has a molar ratio Ti/Al of between 10 to 100, and a molar ratio Mg/Al of between 10 to 600.

[0022] In accordance with the invention, the additive of the present invention may suitably be added to the catalyst ingredients during synthesis of same. Alternatively, the additive of the present invention may suitably be incorporated into the catalyst composition, before or during olefin polymerization.

[0023] In accordance with the invention, the desired additive may be prepared through numerous different methods. In connection with the aluminosiloxane compound additive, the preparation thereof may be accomplished according to K. Folting, W.E. Streib, K.G. Caulton, O. Poncelet and L.G. Hubert-Pfalzgrat, *Polyhedron*, 10 (14), 1639-1646 (1991). A mixture of trimethylsilylacetate and cyclohexene may be added to aluminum isopropoxide in the desired ratio so as to provide the desired relation of Si:Al of 1:1, 2:1 or 3:1. The mixtures so formed are then subjected to isotropic distillation so as to obtain cyclohexene/isopropylacetate, and the solution can then be concentrated and distilled so as to provide

the desired additive. Azeotropic distillation may be carried out at a temperature of approximately 80°C and for a time period of between about 8 to about 24 hours. Of course, the time and temperature of the procedure may be adjusted to particular conditions and ingredients. The resulting additive product may suitably be identified and confirmed to possess the desired structure through IR and ¹H NMR spectroscopies.

[0024] An aluminosiloxane compound $[Al(O^iPr)_2(OSiMe_3)]_m$ according to the invention has spectroscopic information as follows:

IR(cm⁻¹): 1250(Si-C); -1180, 1130 (C-CH₃); 1170; 950 (Si-O); 760; 640 (Al-OR).

¹H NMR (CDCl₃; 0.1 M, 25°C) (ppm): 4.47-4.08 (m, OCHMe₂, 2H). 1.42; 1.27; 1.47; 1.36; 1.21; 1.10; 1.06 (d, J=6Hz, OCHMe₂, 12H); 0.25, 0.22, 0.21 (s, OSiMe₃, 9H)

[0025] While the foregoing provide examples for preparation of additive in accordance with the present invention, it should of course be noted that other processes for preparation of the desired additive may be known to those of ordinary skill in the art and could, of course, be used to prepare the additive of the catalyst of the present invention.

[0026] In further accordance with the invention, a catalyst can be prepared through a synthesis method wherein a mixture of a halogen-containing magnesium compound such as magnesium chloride, a C₄-C₁₂ aliphatic or aromatic solvent such as decane, a C₆-C₁₂ aliphatic or aromatic alcohol such as 2-ethylhexanol and the desired additive is formed. The mixture is preferably charged into a reactor vessel under an inert gas atmosphere, and reacted at an elevated temperature such as approximately 110-140°C for a period of time of approximately 1-4 hours, preferably under stirring. The reaction mixture may then in accordance with the present invention be cooled, preferably to between about 0°C to about -20°C, and a volume of titanium halide such as titanium tetrachloride is slowly added. An additional charge of the desired additive is then added to the mixture, and the mixture is continuously stirred for an additional time period. The mixture is then heated again to an elevated temperature between 60-100°C, for a period of time of 1 to 3 hours, cooled to room temperature and then allowed to settle, and is separated by filtration.

[0027] The separated solid is then preferably suspended in a solution of titanium tetrachloride, heated for another period of time, and resulting solid is again separated for example by filtration. The solid so obtained is then purified, for example by repeated washing with hot hexane, and is then dried under vacuum or inert gas stream. The resulting catalyst is in powder form and preferably has a titanium content of between 3 to 12 wt.%, and an average particle size of between 4 to 100 μm.

[0028] In accordance with the present invention, the above-described process for synthesis has been found to provide catalyst having improved activity. Nevertheless, other methods are of course known in the art for the synthesis of such catalysts, and the catalyst of the present invention could be prepared by such known methods.

[0029] The olefin polymerization catalyst of the present invention can suitably be used for olefin polymerization reactions so as to produce polyolefins such as polyethylene.

[0030] A polymerization reactor may suitably be subjected to evacuation-argon substitution, and then charged with dehydrated and oxygen-removed hexane as well as triethylaluminum and hydrogen so as to prepare the reactor. The reactor may then be saturated with olefins such as ethylene at a working pressure and temperature, for example 8 bar and 80°C, and the catalyst according to the present invention may then be charged into the reactor. After a suitable amount of time, such as, for example, 2 hours, the resulting polymer slurry can be filtered, and a yield of polyolefin such as polyethylene is produced. In accordance with the invention, the polyolefin product preferably has a melt flow index of between 0.01 to 200, and a bulk density of between 0.25 to 0.40. Further, the polymerization according to the present invention using the catalyst of the present invention preferably results in the final polyolefin product having a fines content of less than or equal to 15% of particles having a diameter of less than or equal to 106 μm.

[0031] The following examples further illustrate preparation of additive and catalyst and polymerization in accordance with the invention.

EXAMPLE 1

[0032] The preparation of an aluminosiloxane additive of the formula $[Al(O^iPr)_2OSiMe_3]_m$ was carried out in accordance with the aforementioned reference by K. Folting et al., wherein iPr is isopropyl and Me is methyl. A solution of trimethylsilyl acetate (3.165 g, 0.024 mol) in 0.65 ml of cyclohexane was added to aluminum triisopropoxide (4.93 g, 0.024 mol) over a period of two hours at a temperature of 80°C whereby azeotropic distillation of cyclohexane/isopropyl acetate was achieved. The solution so obtained was then concentrated and distilled at 80°C and 0.01 mm Hg so as to provide additive A, the composition of which was confirmed by IR and ¹H NMR spectroscopies. Two additional additives were also prepared following the same procedures, but altering the Al:Si ratio so as to provide two additional additives: $[Al(O^iPr)(OSiMe_3)_2]_p$ (Additive B); and $[Al(OSiMe_3)_3]_2$ (Additive C).

[0033] The preparation of a catalyst in accordance with the invention using additive A as prepared above was then

carried out. 12.00 g of anhydrous magnesium chloride, 100 ml of decane, 60 ml of 2-ethyl hexanol and 0.25 g of Additive A were charged under an inert gas atmosphere into a reactor vessel and reacted at 120°C for 2 hours. The reaction mixture was cooled to -20°C and then 200 ml of titanium tetrachloride were slowly added. The mixture was stirred for an additional period of 30 minutes, and the temperature of the mixture was then increased to room temperature with occasional stirring and another 0.125 g of Additive A were added, after which the mixture was stirred for an additional 30 minutes.

[0034] The mixture was heated to 90°C for 2 hours and the resulting solid was allowed to settle, was separated by filtration, suspended in 60 ml of titanium tetrachloride and heated at 80°C for 2 hours. The solid was separated by filtration, repeatedly washed with a total volume of hot hexane of about 1000 ml and finally dried under vacuum. The resulting yellow powder showed a titanium content of 8.2% and an average particle size of 14 microns.

EXAMPLE 2

[0035] This example illustrates a polymerization reaction using the catalyst according to the present invention as prepared above in Example 1. A stainless steel autoclave having a stirrer, a temperature controlling device and 2 liter capacity was provided. The reactor was subjected to evacuation-argon substitution several times and was charged with 1 liter of dehydrated and oxygen-removed hexane, 1.68 mmol of triethyl aluminum and 3 bar of hydrogen. The reactor was saturated with ethylene at the working pressure of 8 bar and 80°C, and approximately 10 mg of the catalyst of Example 1 containing Additive A were charged into the reactor. Polymerization was carried out for 2 hours, at which time the resulting polymer slurry was filtered. The process yielded 340 g of polyethylene having a melt flow index of 0.5 g/10 min and a bulk density of 0.25 g/ml. The product had a content of 1.7% of fines having a diameter of less than 106 µm.

EXAMPLE 3

[0036] This example illustrates polymerization carried out according to the invention using a catalyst prepared according to the process of Example 1 using 0.725 g of Additive B instead of the 0.125 g of Additive A. The resulting catalyst was a yellow powder having a titanium content of 7.7% and an average particle size of 11.1 µm.

[0037] Ethylene was polymerized according to the same procedure set forth in Example 2, using the catalyst including Additive B, and the polyethylene yield was 346 g having a melt flow index of 0.57 g/10 min and a bulk density of 0.25 g/ml. The final product contained 2.63% fines having a diameter of less than 106 µm.

Claims

1. An olefin polymerization catalyst, comprising:

a halogen-containing magnesium compound;
a titanium compound; and
an additive selected from the group consisting of

(a) a mixture of an aluminum alkoxide compound and polydimethylsiloxane,
(b) an aluminosiloxane selected from the group consisting of $[Al(OR')_2(OSiR''_3)]_m$, $[Al(OR')(OSiR''_3)_2]_p$,
and $[Al(OSiR''_3)_3]_2$, wherein R' and R'' are alkyl or aryl groups having up to 12 carbons and m and p are
any whole number greater than 1, and mixtures of (a) and (b).

2. A catalyst according to claim 1, wherein said catalyst has a substantially monomodal particle size distribution having an average particle size of between 2 microns and 200 µm.

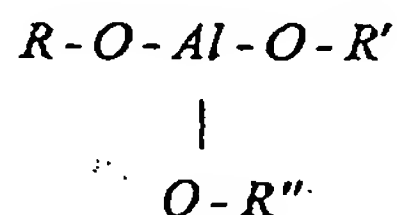
3. A catalyst according to claim 1, wherein said magnesium halide comprises $MgCl_2$ and wherein said titanium compound comprises $TiCl_4$.

4. A catalyst according to claim 1, wherein said additive has an Al/Si molar ratio of between 0.1 and 300.

5. A catalyst according to claim 4, wherein said additive has an Al/Si molar ratio of between 0.33 and 1.

6. A catalyst according to claim 1, wherein said catalyst has a Ti/Al molar ratio of between 10 and 100.

7. A catalyst according to claim 1, wherein said catalyst has an Mg/Al molar ratio of between 10 and 600.
8. A catalyst according to claim 1, wherein said additive comprises a mixture of said aluminum alkoxide compound and said polydimethylsiloxane, and wherein said polydimethylsiloxane has a molecular weight of between 150 and 300,000.
9. A catalyst according to claim 8, wherein said aluminum alkoxide compound is an organic compound having the functionality



wherein R, R' and R'' are hydrocarbyl radicals of not more than 12 carbon atoms.

10. A catalyst according to claim 8, wherein said aluminum alkoxide compound is selected from the group consisting of aluminum methoxide, aluminum ethoxide, aluminum isopropoxide and mixtures thereof.
11. A catalyst according to claim 8, wherein said polydimethylsiloxane has a molecular weight of between 150 to 770.
12. A catalyst according to claim 1, wherein said additive comprises an aluminosiloxane compound.
13. A catalyst according to claim 12, wherein said aluminosiloxane compound is selected from the group consisting of $[Al(OiPr)_2(OSiMe_3)]_m$, $[Al(OiPr)(OSiMe_3)_2]_p$, $[Al(OSiMe_3)_3]_2$, and mixtures thereof wherein m and p are any whole number greater than 1.
14. A catalyst according to claim 1, wherein R' is selected from the group consisting of ethyl, propyl, isopropyl, n-butyl, isobutyl, t-butyl and mixtures thereof, and wherein R'' is selected from the group consisting of methyl, phenyl, ethyl, propyl, isopropyl, t-butyl and mixtures thereof.

Patentansprüche

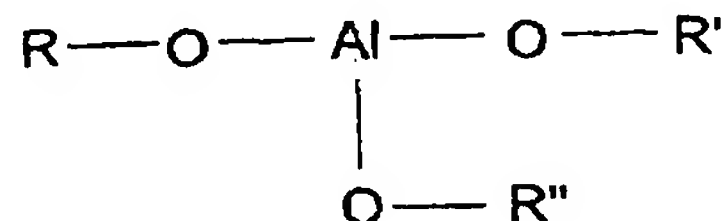
1. Ein Olefin Polymerisationskatalysator enthaltend:

eine halogenhaltige Magnesiumverbindung;
eine Titanverbindung; und
ein Additiv ausgewählt aus der Gruppe bestehend aus

- a) einer Mischung eines Aluminiumalkoxids und Polydimethylsiloxan,
b) ein Aluminosiloxan ausgewählt aus der Gruppe bestehend aus $[Al(OR')_2(OSiR''_3)]_m$, $[Al(OR')(OSiR''_3)_2]_p$, und $[Al(OSiR''_3)_3]_2$, worin R' und R'' Alkyl oder Aryl Gruppen mit bis zu 12 Kohlenstoffen sind und m und p ganze Zahlen größer als 1 sind, und Mischungen von a) und b).

2. Ein Katalysator gemäß Anspruch 1, worin der Katalysator eine im Wesentlichen monomodale Partikelgrößenverteilung mit einer durchschnittlichen Partikelgröße zwischen 2 Mikrons und 200 µm hat.
3. Ein Katalysator gemäß Anspruch 1, worin das Magnesiumhalogenid $MgCl_2$ enthält und worin die Titanverbindung $TiCl_4$ umfasst.
4. Ein Katalysator gemäß Anspruch 1, worin das Additiv ein molares Al/Si Verhältnis zwischen 0,1 und 300 hat.
5. Ein Katalysator gemäß Anspruch 4, worin das Additiv ein molares Al/Si Verhältnis zwischen 0,33 und 1 hat.

6. Ein Katalysator gemäß Anspruch 1, worin der Katalysator ein molares Ti/Al Verhältnis zwischen 10 und 100 hat.
7. Ein Katalysator gemäß Anspruch 1, worin der Katalysator ein molares Mg/Al Verhältnis zwischen 10 und 600 hat.
8. Ein Katalysator gemäß Anspruch 1, worin das Additiv eine Mischung aus das Aluminiumalkoxid und das Polydimethylsiloxan enthält, und worin das Polydimethylsiloxan ein Molekulargewicht zwischen 150 und 300.000 hat.
9. Ein Katalysator gemäß Anspruch 8, worin das Aluminiumalkoxid eine organische Verbindung mit der Funktionalität



ist, worin R, R' und R'' ein Kohlenwasserstoffrest mit nicht mehr als 12 Kohlenstoffatomen ist.

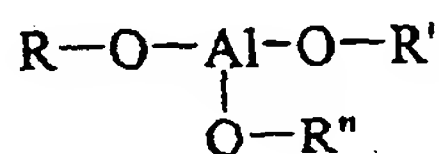
10. Ein Katalysator gemäß Anspruch 8, worin das Aluminiumalkoxid ausgewählt ist aus der Gruppe bestehend aus Aluminiummethoxid, Aluminiumisopropoxid und Mischungen davon.
11. Ein Katalysator gemäß Anspruch 8, worin das Polydimethylsiloxan ein Molekulargewicht zwischen 150 und 770 hat.
12. Ein Katalysator gemäß Anspruch 1, worin das Additiv ein Aluminosiloxan enthält.
13. Ein Katalysator gemäß Anspruch 12, worin das Aluminosiloxan ausgewählt ist aus der Gruppe bestehend aus $[\text{Al}(\text{O}^i\text{Pr})_2(\text{OSiMe}_3)]_m$, $[\text{Al}(\text{O}^i\text{Pr})(\text{OSiMe}_3)_2]_p$, und $[\text{Al}(\text{OSiMe}_3)_3]_2$, und Mischungen davon, worin m und p ganze Zahlen größer als 1 sind.
14. Ein Katalysator gemäß Anspruch 1, worin R' ausgewählt ist aus der Gruppe bestehend aus Ethyl, Propyl, Isopropyl, n-Butyl, Isobutyl, t-Butyl und Mischungen davon, und worin R'' ausgewählt ist aus der Gruppe bestehend aus Methyl, Phenyl, Ethyl, Propyl, Isopropyl, t-Butyl und Mischungen davon.

Revendications

1. Catalyseur de polymérisation d'oléfines, comprenant :
- un composé halogéné du magnésium ;
un composé du titane ; et
un additif choisi dans le groupe constitué
- (a) d'un mélange d'un composé alcoxyde d'aluminium et de polydiméthylsiloxane,
(b) d'un aluminosiloxane choisi dans le groupe constitué de $[\text{Al}(\text{OR}')_2(\text{OSiR}'')_3]_m$, $[\text{Al}(\text{OR}')(\text{OSiR}'')_3]_p$ et $[\text{Al}(\text{OSiR}'')_3]_2$, où R' et R'' sont des groupes alkyle ou aryle ayant jusqu'à 12 atomes de carbone, et m et p sont des nombres entiers quelconques supérieurs à 1, et de mélanges de (a) et de (b).
2. Catalyseur selon la revendication 1, ledit catalyseur ayant une distribution granulométrique essentiellement monomodale, avec une granulométrie moyenne comprise entre 2 et 200 μm .
3. Catalyseur selon la revendication 1, dans lequel ledit halogénure de magnésium comprend du MgCl_2 et ledit composé du titane comprend du TiCl_4 .
4. Catalyseur selon la revendication 1, dans lequel ledit additif présente un rapport en moles Al/Si compris entre 0,1 et 300.

EP 0 810 235 B1

5. Catalyseur selon la revendication 4, dans lequel ledit additif présente un rapport en moles Al/Si compris entre 0,33 et 1.
6. Catalyseur selon la revendication 1, ledit catalyseur présentant un rapport en moles Ti/Al compris entre 10 et 100.
7. Catalyseur selon la revendication 1, ledit catalyseur présentant un rapport en moles Mg/Al compris entre 10 et 600.
8. Catalyseur selon la revendication 1, dans lequel ledit additif comprend un mélange dudit composé alcoxyde d'aluminium et dudit polydiméthylsiloxane, et dans lequel ledit polydiméthylsiloxane a une masse moléculaire comprise entre 150 et 300 000.
9. Catalyseur selon la revendication 8, dans lequel ledit composé alcoxyde d'aluminium est un composé organique ayant la fonctionnalité



dans laquelle R, R' et R'' sont des radicaux hydrocarbyle n'ayant pas plus de 12 atomes de carbone.

10. Catalyseur selon la revendication 8, dans lequel ledit composé alcoxyde d'aluminium est choisi dans le groupe constitué du méthylate d'aluminium, de l'éthylate d'aluminium, de l'isopropylate d'aluminium, et de mélanges de ceux-ci.
11. Catalyseur selon la revendication 8, dans lequel ledit polydiméthylsiloxane a une masse moléculaire comprise entre 150 et 770.
12. Catalyseur selon la revendication 1, dans lequel ledit additif comprend un composé aluminosiloxane.
13. Catalyseur selon la revendication 12, dans lequel ledit composé aluminosiloxane est choisi dans le groupe constitué de $[\text{Al}(\text{O}^i\text{Pr})_2(\text{OSiMe}_3)]_m$, $[\text{Al}(\text{O}^i\text{Pr})(\text{OSiMe}_3)_2]_p$ et $[\text{Al}(\text{OSiMe}_3)_3]_2$, et de mélanges de ceux-ci, où m et p sont des nombres entiers quelconques supérieurs à 1.
14. Catalyseur selon la revendication 1, dans lequel R' est choisi dans l'ensemble constitué de groupes éthyle, propyle, isopropyle, n-butyle, isobutyle, tert-butyle et de mélanges de ceux-ci, et R'' est choisi dans l'ensemble constitué de groupes méthyle, phényle, éthyle, propyle, isopropyle, tert-butyle, et de mélanges de ceux-ci.

fig-1

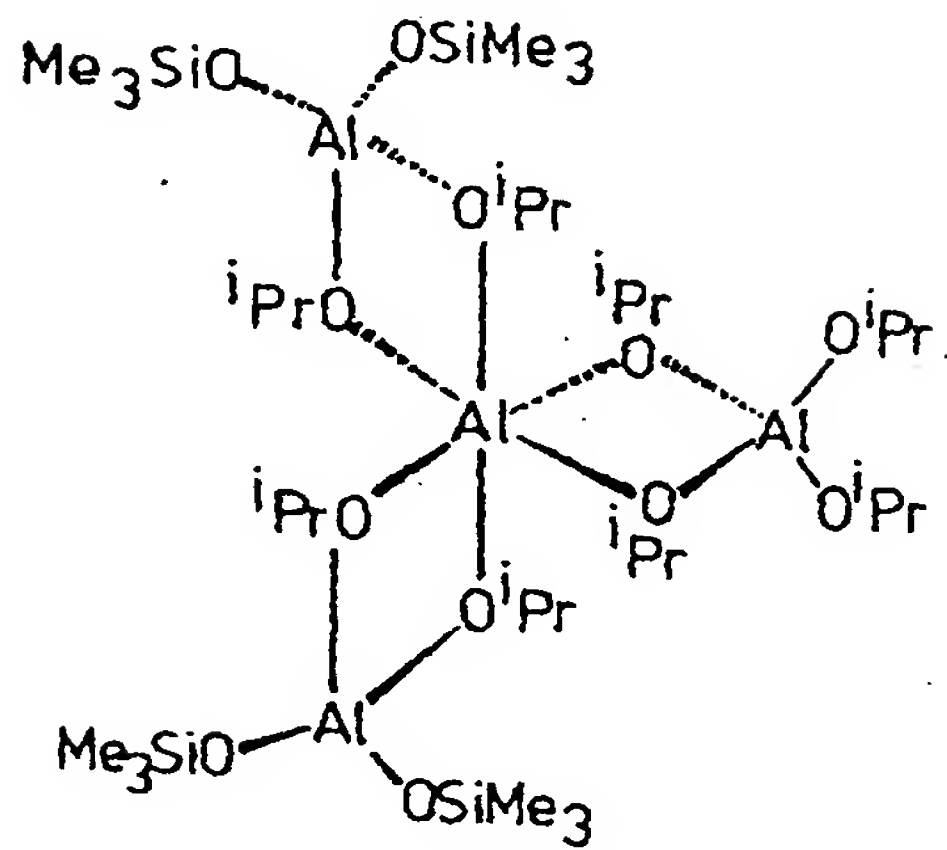


fig-2

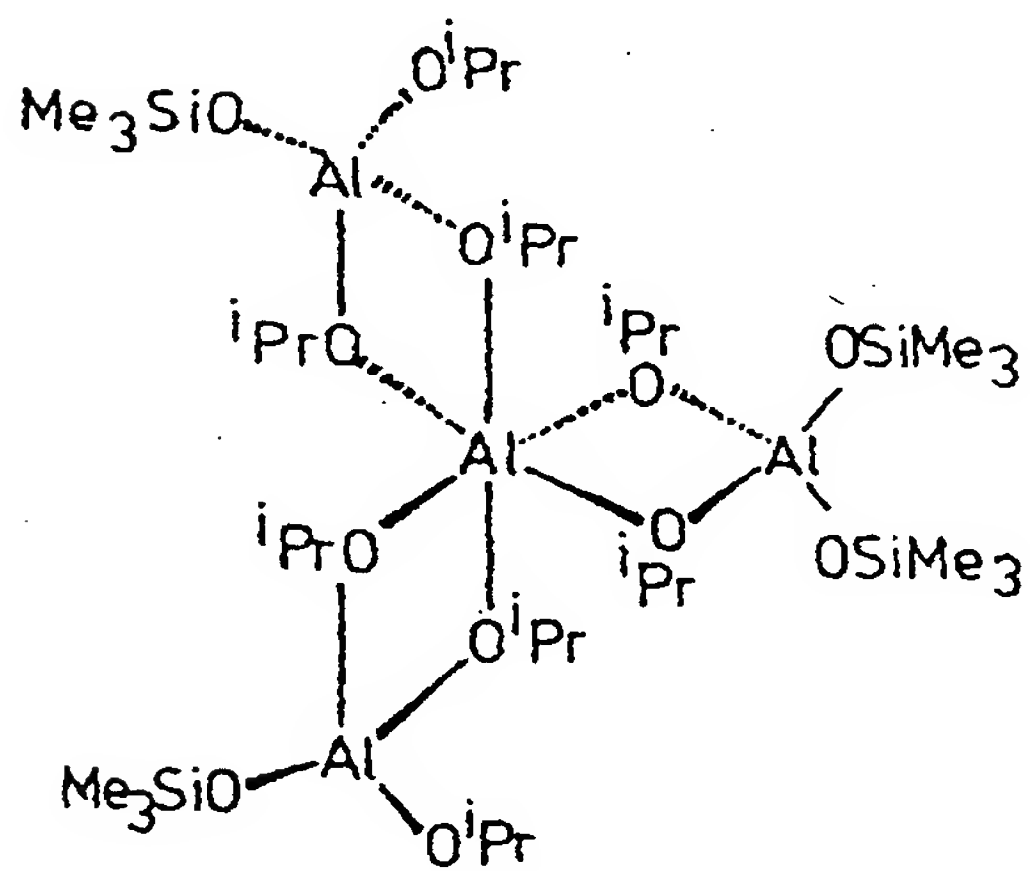


fig-3

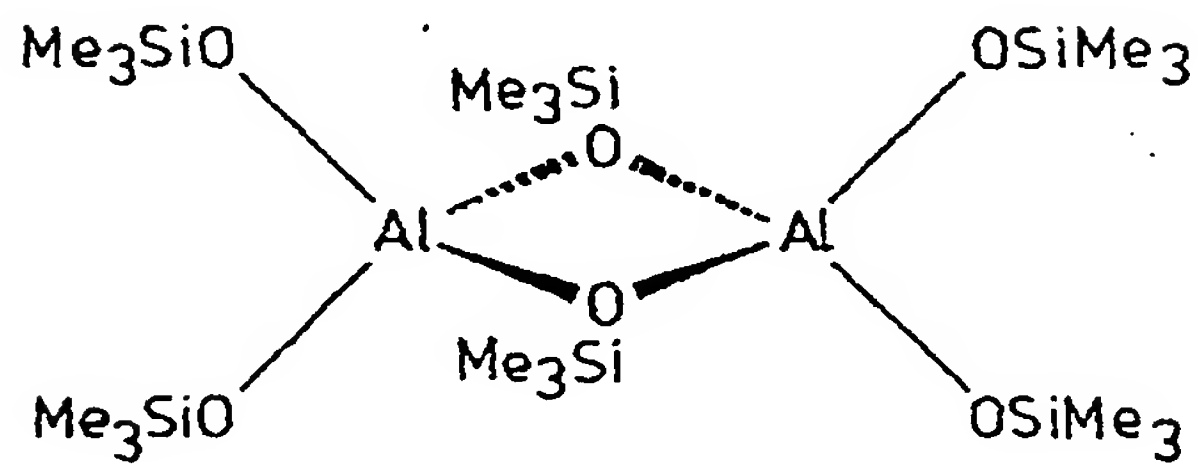


fig - 4

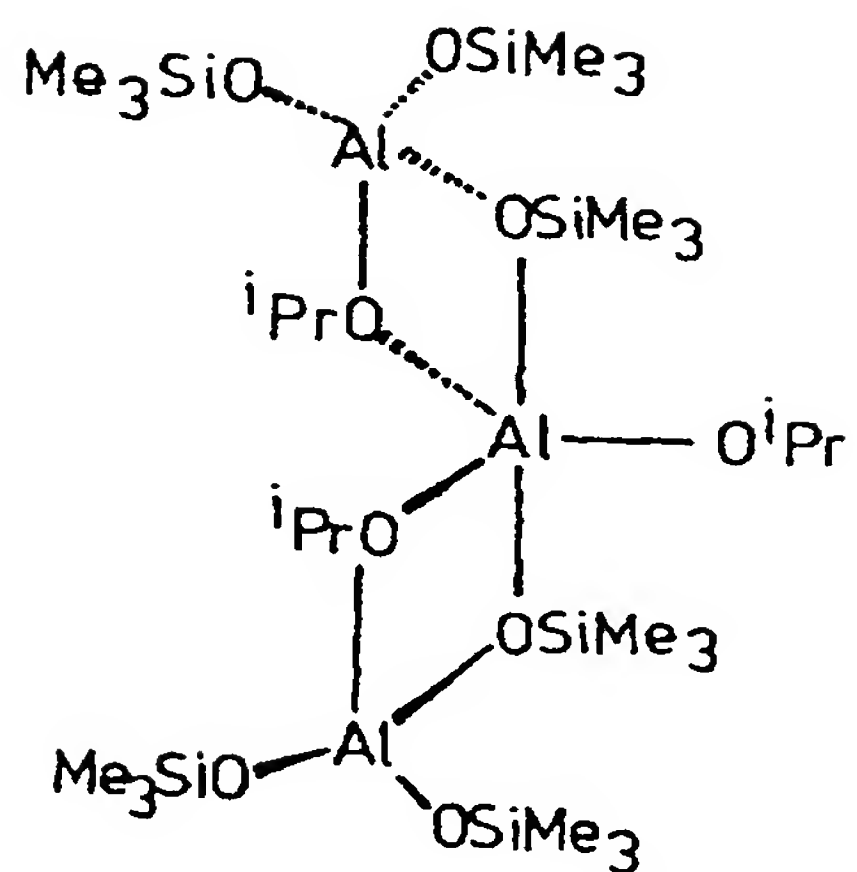


fig-5

